

# Millimeter-wave Chirality Spectrometer (ChiralSpec)

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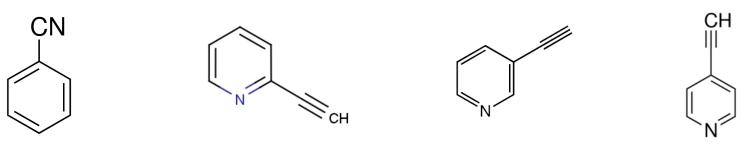


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#### Overview of ChiralSpec



- **Instrument description**: a simple mm-wave spectrometer operated in two modes:
  - Chirality detection mode to determine which enantiomer is in excess
  - Survey mode as a traditional mm-wave spectrometer to characterize chemical composition
- Chirality detection theory formulated in 2012 by Hirota and experimentally demonstrated by groups in Harvard and Virginia at 2-18 GHz with large instruments
- **Goal of this effort**: experimental demonstration of chirality detection at 75-205 GHz where there is a path for instrument miniaturization.
- Addresses planetary science objectives by looking for biosignature patterns: chirality of amino acids; double-bond position in fatty acids; amino acids distribution, etc.
- Complimentary to mass spectrometer for distinguishing isomers of the same molecular weight, e.g., C<sub>7</sub>H<sub>5</sub>N, 103 Da, interesting to Titan, where is N inserted to? What is arrangement of atoms?



Benzonitrile

2-Ethynylpyridine

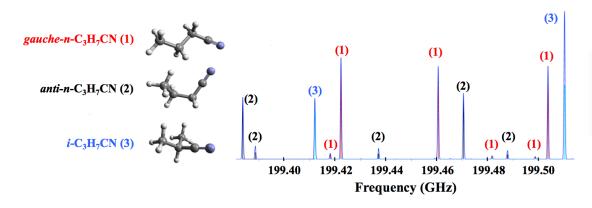
3-Ethynylpyridine

4-Ethynylpyridine

## ChiralSpec's core: rotational spectroscopy

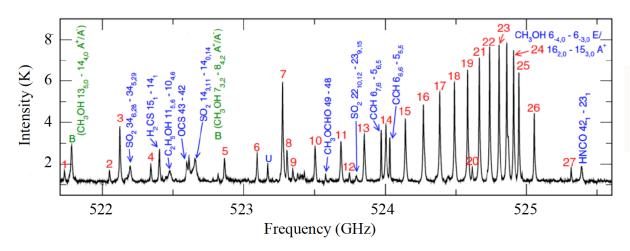


- Non-invasive approach
- Extraordinary capability of distinguishing isomers via high resolving power



Multiple separate lines from each isomer ensure secured identification

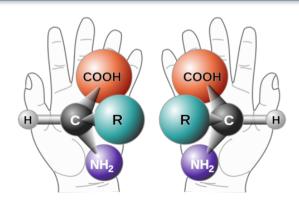
Capable of analyzing mixture of gases without separating them first



Survey spectrum of Orion KL from Herschel/HIFI (red numbers label CH3OH)

#### What is Chirality?





- Enantiomers of a chiral molecule: non-superimposable mirror images
  - Referred in terms of right- and left-handedness
  - Identical in many properties making them challenging to distinguish
  - Indistinguishable by mass spectroscopy
- Can be used as a chemical 'biomarker' for search for life
  - Organisms on Earth use predominately homochiral molecules
  - Life uses only left-handed amino acids
  - Life used only right-handed sugars

#### **Comparative Technologies**

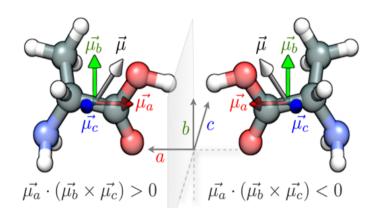


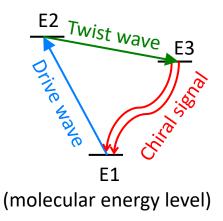
| Technology | Methodology  | Sensitivity   | Comments  |
|------------|--|---|---|
| ChiralSpec | Rotational spectroscopy<br>Targets in gas phase        | Gas: 10 <sup>9</sup> molecules/cm <sup>3</sup> with 1L volume  Solid: ppm level with 0.2mg sample | Not require derivatization Insensitive to non-polar molecules |
| GC-MS      | Gas chromatography Targets in gas phase                | ppm   | Require derivatization  |
| MILA       | Laser induced fluorescence<br>Targets in aqueous phase | Liquid: 100 pM (10 <sup>-10</sup> mol/L)  |   |

- Gas chromatography (GC), implemented in Rosetta/COSAC and Curiosity/SAM
- Microfluidic Life Analyzer (MILA)
  - Capillary electrophoresis-based laser induced fluorescence (CE-LIF)
  - Developed with PICASSO-13 (PI Peter Willis of JPL)
  - With focus on amino and carboxylic acids
  - Measurements involve liquid extraction of samples, fluorescent tagging, introduction of two chiral recognition agents

## Principle of chirality detection by ChiralSpec



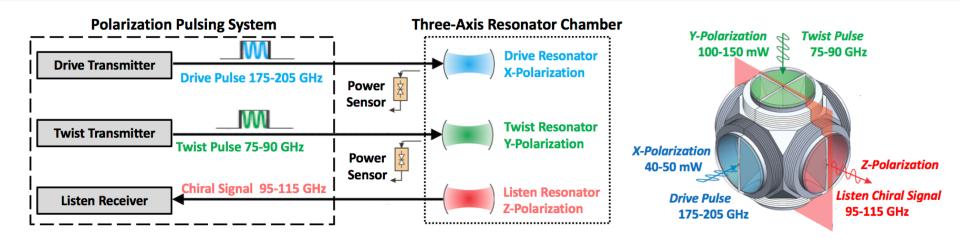




- ✓ Exploiting opposite signs of dipole moment products (Image : Shubert et al 2016)
- $\checkmark$  Simultaneously using a cycle of three transitions involving the a, b and c dipoles
- ✓ Generating a time-domain chiral emission signal via exciting species with two pulses.
- ✓ Enantiomeric pair's chiral signals: same frequency but 180° phase difference

#### Schematic of ChiralSpec instrument





- All three waves capable of tuning frequencies in wide ranges
  - Capable of tuning to molecular fingerprint frequencies
  - Capable of analyzing mixture of gases without separating them first
- Chirality detection mode with all three waves on
  - Enantiomeric pair's chiral signals: same frequency but 180° phase difference
  - Giving difference abundance of enantiomeric pair
- Survey mode with one wave on
  - Giving sum abundance of enantiomeric pair
  - Giving abundance for each of nonchiral molecules

#### Benchmark Molecules



| Molecule  | Cycle | Pulse  | Transition                       | Freq. (GHz)                      |         |
|---|-------|--------|----------------------------------|----------------------------------|---------|
| Propylene Oxide                                     |       | Drive  | $8_{4,4} \leftarrow 7_{3,4}$     | 182.856                          |         |
| (CH₃CHCH₂O)<br>MW=58 g/mol                          | 1     | Twist  | $8_{3,5} \leftarrow 8_{4,4}$     | 81.256                           |         |
| $\mu_a$ , $\mu_B$ , $\mu_c$ =0.95,1.67, 0.56 Debye  |       | Listen | $7_{3,4} \leftarrow 8_{3,5}$     | 101.599                          |         |
|   |       | Drive  | $15_{4,11} \leftarrow 14_{4,10}$ | 191.226                          |         |
| $H_3C_{\prime,}$                                    | 2     | Twist  | $14_{5,10} \leftarrow 15_{4,11}$ | 88.069                           |         |
| O   |       |        | Listen                           | $14_{4,10} \leftarrow 14_{5,10}$ | 103.157 |
| Alanine   |       | Drive  | $21_{17,4} \leftarrow 20_{16,4}$ | 191.590                          |         |
| (CH₃CHNH₂COOH)<br>MW=89 g/mol                       | 1     | Twist  | $21_{16,5} \leftarrow 21_{17,4}$ | 76.855                           |         |
| $\mu_a$ , $\mu_b$ , $\mu_c$ =0.62, 1.33, 0.34 Debye |       | Listen | $20_{16,4} \leftarrow 21_{16,5}$ | 114.735                          |         |
| 0   |       | Drive  | $20_{19,1} \leftarrow 19_{18,1}$ | 195.558                          |         |
| H <sub>3</sub> C OH                                 | 2     | Twist  | $20_{18,2} \leftarrow 20_{19,1}$ | 86.643                           |         |
| $^{ m N}$ H $_{ m 2}$                               |       | Listen | $19_{18,1} \leftarrow 20_{18,2}$ | 108.915                          |         |

- Propylene oxide is the first chiral molecule observed in ISM (McGuire et al 2016), is volatile and easier for sampling handling (vapor pressure of 450 Torr at 300K).
- We will use laser ablation to bring alanine into gas phase.

#### Schedule and Milestones



| Tasks  |                      | 2017 |   |            |  | 2018                     |     |      |      |      |       | 201   |      |      |     |       | 19  | 9               |          |      |       |      | 2020 |      |      |       |      |       |
|--|----------------------|------|---|------------|--|--------------------------|-----|------|------|------|-------|-------|------|------|-----|-------|-----|-----------------|----------|------|-------|------|------|------|------|-------|------|-------|
|  |                      | 23   | ( | <b>)</b> 4 |  | Q1                       |     | Q2   |      | Q3   | I     | Q4    |      | Q1   |     | Q2    |     | Q               | 3        | Q    | 4     | (    | Q1   |      | Q2   |       | Q3   | Q4    |
| T1 Design, fabricate, integrate & test pulsing system        |                      |      |   |            |  |                          |     |      |      |      |       |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 1.1 Drive pulse amplifier design,fabrication and test        | ~50mW achieved or th |      |   |            |  | or the drive pulse power |     |      |      |      |       |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 1.2 Phase-trigger circuit design, fabrication and test       |                      |      |   |            |  |                          |     |      |      |      |       |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 1.3 procurement  |                      |      |   |            |  |                          |     |      |      |      |       |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 1.4 Pulsing system integration and test                      |                      |      |   |            |  |                          |     |      |      |      | I     | •     | 1    | rad  | ian | pre   | cis | ion             | acł      | niev | ed    | for  | pha  | se   | mea  | asur  | eme  | nts   |
| T2 Design, fabricate, integrate & test resonator/coupler     |                      |      |   |            |  |                          |     |      |      |      | Τ     |       |      |      |     |       |     |                 | <b>•</b> | Q ≥  | ≥10   | 00   | ach  | eve  | ed f | or re | son  | ators |
| T3 Advance mm-wave three-wave mixing technology              |                      |      |   |            |  |                          |     |      |      |      | Τ     |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 3.1 Measure chirality of propylene oxide without resonators  |                      |      |   |            |  |                          |     |      |      |      | Т     |       |      |      |     |       |     |                 | •        | Chi  | rali  | ty r | nea  | sur  | ed f | or R  | &S   | samp  |
| T4 Advance mm-wave cavity resonance technology               |                      |      |   |            |  |                          |     |      |      |      |       |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 4.1 Measure chirality of propylene oxide with resonators     |                      |      |   |            |  | 100                      | 00x | chir | al : | sens | i ⁄it | y in  | cre  | aser | me  | nt a  | che | eive            | d        |      |       |      | •    |      |      |       |      |       |
| T5 Demonstrate ChiralSpec applicability to missions          |                      |      |   |            |  |                          |     |      |      |      | Τ     |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 5.1 Measure chirality of R-propylene oxide                   |                      |      |   |            |  |                          |     |      | С    | hira | l si  | gnal  | ob   | ser  | /ec | for   | 10  | <sup>-5</sup> m | ιΤοι     | rr R | -sar  | mpl  | е    |      |      |       |      |       |
| 5.2 Measure chirality of mixture of R- and S-propylene oxide |                      |      |   |            |  | Chi                      | ral | sigr | nal  | obse | e ve  | ed fo | or 1 | 0-4  | mΤ  | orr s | san | nple            | wit      | h di | ffere | ent  | R:S  | rati | ios  | •     |      |       |
| 5.3 Set up laser ablation sample handling system             |                      |      |   |            |  |                          |     |      |      |      | I     |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 5.4 Measure chirality of pure alanine ice                    |                      |      |   |            |  |                          |     |      |      |      |       |       |      |      |     |       |     |                 |          |      |       |      |      |      |      |       |      |       |
| 5.5 Measure chirality of alanine-impregnated water ice       |                      |      |   |            |  |                          | С   | hira | l si | gnal | of    | alar  | nine | e ob | sei | ved   | at  | 771             | √ in     | ala  | nin   | ie-i | mpr  | egn  | ate  | d wa  | iter | ice   |

## Acknowledgements



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